

Displacement of Crude Oil and Benzene from Silica by Aqueous Solutions

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

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F. Laverne Miller

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Ann Arbor

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INTRODUCTION

The object of this investigation has been to obtain data which would give information concerning the function of "flooding agents" used in the displacement of oil from oil-bearing sands. The results obtained indicate that neither the surface-tension values of the liquids nor the interfacial-tension values of the liquid-liquid system are the dominant factors. Effective displacing agents appear to be those that alter the aqueous solution-silica interface either through a high degree of adsorption or through chemical reaction at the interface.

IN AN earlier paper the authors (2) reported some results obtained in a study of the displacement of different crude oils from finely powdered and compressed silica by water. A determination of the percentage of oil which could be recovered from oil-wetted silica was not attempted, but the magnitude of the pressures developed in the displacement of the oils from silica was determined. In the present paper the problem of the displacement of oil by aqueous solutions is considered.

It is well known that water will displace organic liquids and

crude petroleum oils from silica. It has been observed, however, that water itself is comparatively ineffective as a displacing agent when used in actual oil-field work. The water, whose displacing ability is originally very effective, soon becomes sluggish in its action, and the rate of displacement of the oil becomes low. This effect may be due in part to the saturation of water with some of the more soluble constituents of the oil or to highly adsorbed constituents of the oil on the silica surface which are not easily removed by the water. Experience has shown that certain aqueous solutions are more effective than pure water in removing the oil from the silica. Such solutions are generally known as flooding agents. The salt solution most commonly referred to in this connection is sodium carbonate, or soda ash. Practically, the use of this salt has apparently not met with success. Uren (15) and Beckstrom and Van Tuyl (8) have used a number of different salt solutions in their researches and have determined the relative percentages of oil recovered by each. Uren and Fahmy (16) have also recently published data showing the effect of different salt solutions upon the recovery of crude oils by displacement. It is the opinion of the above-mentioned workers that only the salts of strong bases and weak acids are effective as flooding agents. Acidic salts or neutral salts are not suitable.

THEORIES RELATING TO FUNCTION OF FLOODING AGENTS

A number of theories have been advanced to explain the behavior of such aqueous solutions, but as yet none of them is generally accepted. It has been suggested that the oil is displaced from the sand because of a differential capillary effect; i. e., since the water has a higher surface tension than the oil, it was thought that the difference in these capillary forces might result in the displacement of the oil. Salts, which when added to water cause an increase in the surface tension of the water, would, then, produce a greater difference between the two surface tensions and would thus effect a greater displacement of the oil from the sand. This explanation is hardly acceptable in view of the fact that many different salts will increase the surface tension of water, and yet only a few of them are efficient as flooding agents. It is also true that the increase in surface tension of the water is slight.

Other investigators have attributed the displacement tendency to a chemical reaction. Nutting (11-14) is one who has advanced this idea. He suggested that an attraction exists between the silica particles (SiO_2) and the hydrogen ions of the water, so that a layer of siloxyl (SiOOH) radicals is formed. These radicals would be acidic in character and would have one free bond by means of which they might unite with some other substance. A reaction between the siloxyl radicals and the basic constituents of the oil then would occur, so that over the surface there would be a chemical combina-

tion of the oil with silica which is quite stable. If pure water alone were used as a flooding agent, the displacement of oil would not be efficient because of the formation of this compound. If, however, some alkaline salt were added, the oil would be much more completely displaced; the strong base would displace the weaker one from the acidic siloxyl radical, and the oil, being weakly basic, would thus be removed. This would leave on the surface of the silica grains a coating of MHSiO_3 ($\text{M} = \text{Na}, \text{K}, \text{etc.}$) instead of the oil compound.

Another theory, which depends upon a physical interpretation, has been advanced to explain the displacement of oil by water and its solutions. It is assumed that the oil removal is accomplished by means of a rearrangement of the interfacial-tension relationships between water, oil, and silica. Certain simple relationships between the interfacial forces

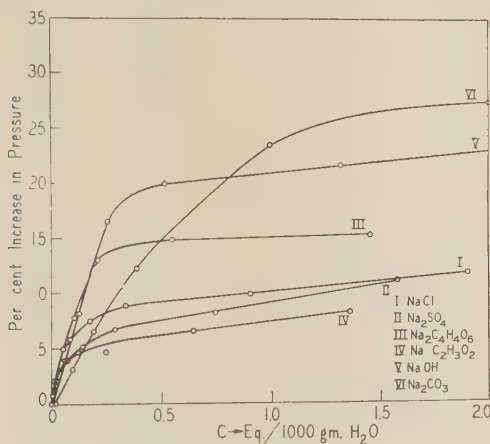


FIGURE 1. INCREASE IN PRESSURE, BENZENE-AQUEOUS SOLUTIONS

will determine the direction of the displacement. Let S_{12} represent the interfacial tension, oil-solid; S_{13} the interfacial tension, water-solid; and S_{23} the interfacial tension, water-oil. Consider that the following relationship holds when

$$S_{12} > S_{13} + S_{23}$$

that is, when S_{12} is greater than the sum of the other two interfacial tensions, the oil-solid (S_{12}) interface will be the one to disappear. This is found to be the case with silica as the solid; the organic liquids and oils are displaced by water. There are no reliable methods for measuring either S_{12} or S_{13} , but there are a number of different methods for determining accurately the value of the interfacial tension, liquid-liquid (S_{23}), and it is known also that it is possible to alter its value. Uren (15, 16) noted that the addition of sodium carbonate would lower the interfacial tension of a water-oil system from about 18 dynes per cm. to 6 dynes per cm. or less, as measured

by the ring method. While the relationship given above is theoretically sound, it cannot be applied on a quantitative basis, owing to the lack of interfacial-tension data relating to solid-liquid systems.

It is believed by some investigators that the displacement is really the result of the combination of the two factors—chemical combination and interfacial tension. In this case, reaction is considered to occur between the silica and the alkali (sodium hydroxide, potassium hydroxide, etc.) which is added or which is formed by the hydrolysis of strongly basic salts. Uren (15, 16) has recently expressed the belief that the reaction between the silica and sodium hydroxide forms a silicate which is soluble, and the factor S_{13} in the equation above consequently becomes zero. It seems impossible to determine the correctness of this view inasmuch as so little is known concerning the true value of the interfacial

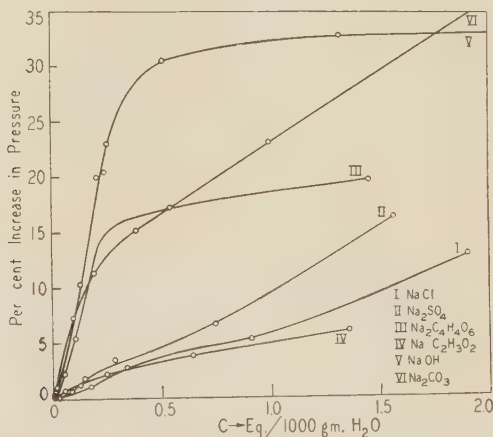


FIGURE 2. INCREASE IN PRESSURE, CRUDE OIL-AQUEOUS SOLUTIONS

tension of the solid-liquid system. The above author also believes it possible that a reaction between the base and the oil is the cause of the reduction of the interfacial tension, oil-aqueous solution, so that both of the interfacial tensions, S_{13} and S_{23} , may be considered to have been decreased as a result of chemical reactions. Thus it is believed that salt solutions are effective as flooding agents in proportion to the amount of base they are able to furnish the solution.

In order to obtain further information regarding the displacement of oils from sands, it seemed desirable to carry out an investigation with silica and crude oils, in which would be measured the maximum displacement pressure of oil by different aqueous solutions over a wide range of concentrations and also the interfacial tension values of these same solutions against the oil. In addition, it seemed desirable to use some pure organic liquid (one non-reactive with alkali) in

the place of the oil, and to make similar measurements with the aqueous solutions. In this manner it should be possible to observe the similarities or the dissimilarities in the behavior of systems in which a chemical reaction was possible, and one in which no reaction was known to occur. A comparison of results obtained with the crude oil and with the organic liquid should, it seemed, give worthwhile information concerning the displacement of oils from sands.

TABLE I. DISPLACEMENT OF CRUDE OIL M AND BENZENE BY AQUEOUS SOLUTIONS

CONCENTRATION		BENZENE Increase in pressure			CRUDE OIL Increase in pressure		
% by wt.	Equiv./M grams H_2O	Pressure Grams/ cm. ²	S_{23}		Pressure Grams/ cm. ²	S_{23}	
NaCl							
0.00	0.0000	346.5	0.0	34.65	255.3	0.0	24.54
0.05	0.0085	349.3	0.8	34.71	255.3	0.0	24.93
0.10	0.0171	353.3	2.1	34.75	255.3	0.0	25.07
0.50	0.0859	366.9	5.9	34.91	256.8	0.6	25.49
1.00	0.1728	372.4	7.5	35.10	258.0	1.0	25.67
2.00	0.3395	377.3	8.9	35.40	262.3	2.7	25.87
5.00	0.9014	380.5	9.8	36.20	268.5	5.2	26.13
10.00	1.9010	387.3	11.8	37.40	288.1	12.8	26.27
Na_2SO_4							
0.00	0.0000	346.5	0.0	34.65	255.3	0.0	24.54
0.10	0.0141	346.5	0.0	34.71	255.3	0.0	24.54
0.20	0.0282	353.5	2.1	34.80	255.3	0.0	24.54
0.50	0.0708	360.1	3.9	34.95	256.8	0.6	24.54
1.00	0.1423	364.2	5.1	35.10	260.0	1.8	24.54
2.00	0.2874	369.7	6.7	35.25	264.0	3.4	24.55
5.00	0.7422	375.1	8.2	35.78	272.0	6.5	24.60
10.00	1.5650	384.6	11.2	36.70	296.4	16.1	24.73
$Na_2C_2H_3O_2$							
0.00	0.0000	346.5	0.0	34.65	255.3	0.0	24.54
0.50	0.0613	360.1	3.9	34.62	256.9	0.6	23.58
1.00	0.1232	362.9	4.7	34.68	258.2	1.1	23.10
2.00	0.2489	362.9	4.7	34.71	260.9	2.2	22.36
5.00	0.6427	368.3	6.3	34.68	265.0	3.8	18.99
10.00	1.3550	375.1	8.2	34.75	270.4	5.9	12.85
$Na_2C_4H_4O_6$							
0.00	0.0000	346.5	0.0	34.65	255.3	0.0	24.54
0.50	0.0518	364.2	5.1	34.45	260.9	2.2	24.54
1.00	0.1041	373.7	7.8	34.33	269.0	5.4	24.54
2.00	0.2104	391.8	13.1	34.11	305.8	19.8	24.45
5.00	0.5432	398.2	14.9	34.02	299.0	17.1	23.99
10.00	1.1454	399.5	15.3	34.27	304.2	19.6	22.24
Na_2CO_3							
0.00	0.0000	346.5	0.0	34.65	255.3	0.0	24.54
0.01	0.0019	346.5	0.0	34.10	255.3	0.0	23.29
0.05	0.0094	346.5	0.0	34.12	256.8	0.6	15.62
0.10	0.0189	346.5	0.0	34.17	258.0	1.0	13.69
0.50	0.0948	357.9	3.2	34.33	273.4	7.1	9.32
1.00	0.1906	369.1	6.5	34.51	284.0	11.2	7.06
2.00	0.3850	389.2	12.3	34.64	293.5	15.0	2.54
5.00	0.9942	428.1	23.5	34.75	313.9	23.0	1.19
10.00	2.0960	441.7	27.4	34.85	346.5	35.8	1.02
NaOH							
0.00	0.0000	346.5	0.0	34.65	255.3	0.0	24.54
0.052	0.01	...	...	33.76	...	...	...
0.50	0.1256	375.1	8.2	34.10	281.3	10.2	9.08
1.00	0.2525	403.6	16.5	34.40	313.6	22.9	8.52
2.00	0.5102	415.9	20.0	35.05	332.9	30.4	8.26
5.00	1.3170	421.3	21.6	35.90	338.4	32.6	8.10
5.24	1.380	...	...	35.95	...	...	...
10.00	2.7780	432.2	24.7	36.05	339.8	33.2	6.91

MATERIALS AND METHODS USED

In carrying out the measurements indicated above, a crude oil, referred to as crude oil M in a previous paper (2), and benzene were the two liquids used. The crude oil appeared to be representative of crude oils in general, and its properties were admirably suited to this type of work. The salts chosen for this investigation were NaCl, Na_2SO_4 , $\text{NaC}_2\text{H}_3\text{O}_2$, $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$, Na_2CO_3 ; and the base, NaOH. These were used in concentrations ranging from about 0.1 to 10 per cent by weight. The silica used in this investigation was air-float Tripoli silica of about 350-mesh particle size which had been purified by hydrochloric acid treatment until it analyzed less than 0.4 per cent impurities.

The interfacial tensions of the aqueous solutions against benzene and against the crude oil were determined by means of a method developed by the authors which has been described in previous papers (2, 3). This method is based upon a modification of the capillary-tube method and is well suited to work with oil which may be dark and not transparent. The measurements were carried out in a thermostat which was maintained at 25° C.

For measuring the displacement of benzene and the oil by the aqueous solutions, the cell designed by Bartell and Osterhof (5) was used. This method has been described in a number of recent papers (1, 2, 4, 5, 6, 7), so that it will be unnecessary to give further details at this time. With the apparatus it is possible to measure the maximum pressure developed when water or an aqueous solution tends to displace another and immiscible liquid from silica. The actual amount of oil or benzene displaced was not measured.

NOTE. The cells were packed by means of a hydraulic press under a gage pressure of 3000 pounds per square inch (210.9 kg. per sq. cm.). Recent work in this laboratory has shown, however, that under such conditions the effective pore size of the membrane may vary somewhat with progressive displacement of liquid. No attempts, therefore, have been made to use the displacement data obtained in this work in calculating the adhesion tension values for these solutions. Since the conditions are probably quite comparable with those found in the actual oil sands, the pressure data are given to show the effect of the different salt solutions upon the displacement of the oil.

DISPLACEMENT PRESSURES

From the displacement-pressure measurements with the oil and benzene against the different aqueous solutions, some interesting relationships were observed. With dilute solutions of salts such as NaCl and Na_2SO_4 , the maximum displacement pressures were only slightly different from those obtained with pure water. When solutions of 10 per cent concentration were used, the total pressure increase was 11.8 and 12.8 per cent (Table I) for benzene and crude oil, respectively, with NaCl; and 11.2 and 16.1 per cent for the same pair of liquids with Na_2SO_4 . There was very little increase in pressure when $\text{NaC}_2\text{H}_3\text{O}_2$ solutions were employed.

With a 10 per cent solution of this salt the pressure increase amounted to 8.2 per cent for benzene and 5.9 per cent for the oil. When $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ was used, however, somewhat greater pressure differences were obtained. The increases in pressures were 15.3 and 19.6 per cent for the benzene and oil, respectively, with a 10 per cent solution. With Na_2CO_3 and NaOH solutions the greatest effects were obtained. A 10 per cent solution of Na_2CO_3 caused an increase in pressure of the benzene displacement of 27.4 per cent and an increase of 35.8 per cent in the pressure of displacement of the oil. A similar concentration of NaOH caused increases of 24.7 and 33.2 per cent, respectively, for the same two liquids. It is interesting to note that the percentage increase of pressures is very similar with both benzene and the crude oil against the various solutions. This series of pressure measurements also shows an agreement with the views of other workers—namely, that alkaline solutions are the most effective in displacing oils from oil-bearing sands. Graphs showing the relation of concentration of salt solutions to percentage increase in pressure are given in Figures 1 and 2.

INTERFACIAL-TENSION VALUES

The results of the interfacial-tension measurements of the different solutions against crude oil and against benzene are more striking than those of pressure measurements. With solutions of the neutral salts, such as NaCl and Na_2SO_4 , no great difference in the liquid-liquid interfacial-tension values were observed. Against benzene, both salt solutions increased the interfacial-tension values until at a concentration of 10 per cent the values were 37.4 and 36.7 dynes per cm. for NaCl and Na_2SO_4 solutions, respectively, which compare with 34.65 dynes per cm. for the water-benzene interface (Table I). With the crude oil, similar increases were obtained although they were not quite so great as those found with benzene. With $\text{NaC}_2\text{H}_3\text{O}_2$, however, the benzene and crude oil behaved quite differently (Table I). Against benzene there was little if any change in the interfacial-tension values even at rather great concentrations of solute. Against the crude oil the salt solution reduced the interfacial-tension value almost 50 per cent when a 10 per cent salt solution was used. $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ solutions seemed to behave almost the same against both of the liquids. A small decrease in the interfacial tension against both benzene and the crude oil was observed (Table I). With the NaOH and Na_2CO_3 solutions, however, there was no similarity between the effect upon the benzene-water tension and upon the crude oil-water tension. Against the crude oil a 10 per cent solution of NaOH reduced the interfacial tension from a value of 24.54 dynes per cm. to 6.91 dynes per cm. With Na_2CO_3 a still greater decrease was obtained. The interfacial tension of a 10 per cent solution against the crude oil was found to be around 1 dyne per cm. In both of these systems the interfacial-tension values dropped

very rapidly with increasing concentration of the salt or base (curves V and VI, Figure 3). Against benzene, quite different results were obtained. At low concentrations, only slight decreases in the interfacial tensions of the solutions against benzene were found. With a Na_2CO_3 solution of 0.010 per cent concentration, the interfacial tension was found to be 34.10 dynes per cm. compared with 34.65 for benzene-water. With higher concentration the values increased regularly until at a concentration of 10 per cent the value was 34.85 dynes per cm. With NaOH a similar result was obtained. With a concentration of 0.052 per cent the value found was 33.76 dynes per cm., but, as the concentration was increased, the interfacial-tension values increased until at a concentration of 5.24 per cent the value found was 35.95 dynes per cm. These measurements agree fairly well with those obtained by Harkins and co-workers (9) in which they found with the drop-weight method that at low concentrations a decrease of 1 to 2

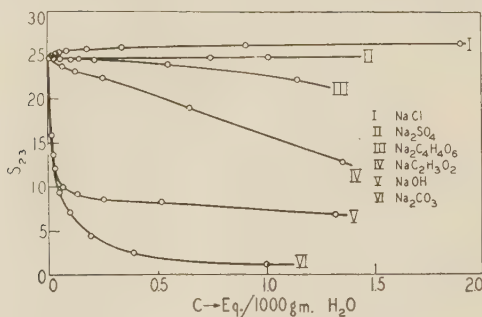


FIGURE 3. INTERFACIAL TENSION, CRUDE OIL-AQUEOUS SOLUTIONS

per cent was observed in the sodium hydroxide-benzene interfacial tension, although increasing the concentration soon caused the tension to go higher than that of water-benzene. In Figures 3 and 4 curves are presented to show the effect of the different salt solutions upon the interfacial tensions of the benzene-water and crude oil-water interface.

NOTE. The NaOH used for the above measurements was prepared by allowing water vapor to come into contact with metallic sodium. The resulting concentrated solution was caught in a platinum dish below a monel-metal gauze upon which the sodium was suspended. This NaOH gave excellent results which were easily reproducible. Measurements which were attempted with some of the purified compound obtained from various commercial sources did not give satisfactory results, nor results which could be duplicated.

DISCUSSION

From the results obtained above it appears that several relationships exist between the effect of aqueous solutions upon benzene and crude oil, and their displacement from silica by these solutions. As a result of the displacement-

pressure determinations, one obtains evidence that the different salt solutions behave similarly against both benzene and crude oil. This is difficult to explain in the light of some of the earlier theories. It is also obvious that the alkaline solutions are more effective in bringing about this displacement.

Interfacial-tension measurements show that the effect of the neutral salt solutions against benzene and oil is similar, but that with alkaline solutions the effect upon the two liquids is very different. Alkaline solutions greatly reduce the interfacial tension of the water-crude oil interface whereas they increase slightly the water-benzene interfacial tension. This would indicate that the alkaline substances must react with some constituent of the crude oil, so that a compound is formed which is highly adsorbed at the liquid-liquid interface. This then would cause the great decrease in the interfacial tension which has been observed. It would appear, however, that this reaction between the oil and alkali does not have an

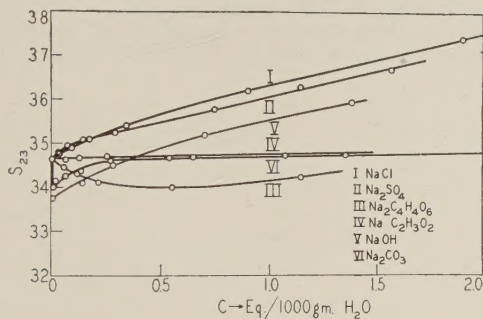


FIGURE 4. INTERFACIAL TENSION, BENZENE-AQUEOUS SOLUTIONS

appreciable effect upon the displacement of oil from the sand, since the alkaline solutions appear to displace the benzene from the sand just as effectively as they do the oil. It seems probable that the increased effectiveness of the alkaline solutions in displacing liquids from silica is due to a reaction between the silica and the aqueous solution. Either the base reacts chemically with the silica or is highly adsorbed by it. The factor determining the efficiency of flooding agents then appears to be associated with the aqueous solution-silica portion of the system. In this respect the views of Nutting (10, 13, 14) receive, at least, partial substantiation. According to his theory, effective oil displacement by aqueous solutions is brought about by chemical reactions which occur at the solid-liquid interface. His views were discussed earlier in this paper.

As a result of the present investigation, it may be concluded that whatever the nature of the displacement no definite relationship between the change in pressure of displacement and the change in the liquid-liquid interfacial-tension values

can be found. Effective displacing agents appear to be those that alter the aqueous solution-silica interface, either through a high degree of adsorption or through chemical reaction at the interface.

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